From fluctuations in hydrodynamics to nonequilibrium thermodynamics

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This paper reports on a macroscopic fluctuation theory developed over the last ten years in collaboration with L. Bertini, A. De Sole, D. Gabrielli and C. Landim. This theory has been inspired by and tested on stochastic models of interacting particles (stochastic lattice gases). It is the basis for a new approach to the study of stationary non equilibrium states applicable to a large class of systems. This overview emphasizes general ideas and for the details I refer to the published papers.

§1. Introduction

I will start with a question: why is the theory of irreversible processes so much more difficult than the theory of equilibrium phenomena? Here are some reasons.

In equilibrium we do not have to solve any equation of motion and the Gibbs distribution provides the basis for the calculation of macroscopic quantities and their fluctuations. In nonequilibrium we cannot bypass the dynamics even in the study of stationary states which we may consider as the simplest beyond equilibrium. It is easy to write down the equation for the stationary ensemble once we know the microscopic dynamics, but the solution is in general very hard to find. Out of equilibrium therefore the basic object to define analogs of entropy or thermodynamic potentials which we need to construct a natural extension of thermodynamics, is not immediately available.

Since the first attempts to develop a nonequilibrium thermodynamics a guiding idea has been that of local equilibrium. This means the following. One assumes that locally on the macroscopic scale it is possible to define variables like density, temperature, chemical potentials... which vary smoothly on this scale. Microscopically this implies that locally the system reaches equilibrium in a time which is short compared to the times typical of macroscopic evolutions as described for example by hydrodynamics. So what characterizes situations in which this description applies is a separation of scales both in space and time.

A theoretical laboratory where to test this idea is provided by stochastic lattice gases which in the last decades have been intensely studied. For several models local equilibrium has been proved and hydrodynamic evolution equations have been derived. The microscopic dynamics of these models is different from the Hamiltonian dynamics that one would assume for a classical real gas but the hope is that the macroscopic behavior of a system, at least for certain intervals of time, be qualita-

tively independent of this assumption. We expect that general properties like the type and number of conservations laws should be the most relevant features.

An important achievement in the study of lattice gases has been the analysis of hydrodynamical fluctuations that is the estimate of the probability that the evolution of a macroscopic variable, e.g. the density, deviates from a solution of hydrodynamics. This suggests a dynamical approach to the estimate of the invariant measure in analogy with the Freidlin-Ventzell theory for stochastic differential equations in finite dimension. Let us give for convenience of the reader a sketch of the Freidlin-Ventzell scheme.[1]

Consider a stochastic differential equation

$$dx_t = b(x_t)dt + \epsilon\sigma dw_t, \tag{1·1}$$

where the vector field b is the drift and σ the diffusion matrix. One is interested in the limit $\epsilon \to 0$. Then the following holds: the probability that the solution stay close to a trajectory ϕ_t in a fixed time interval $[0, T]$ is

$$P(x_t \simeq \phi_t) \simeq \exp\left(-\frac{1}{\epsilon^2}I_T(\phi_t)\right), \tag{1·2}$$

where

$$I_T(\phi_t) = \frac{1}{2}\int_0^T dt(\dot\phi - b(\phi_t))\sigma^{-2}(\dot\phi - b(\phi_t)). \tag{1·3}$$

I_T is called the large deviation functional.

From this one obtains the estimate of the stationary distribution in the neighborhood of an equilibrium point

$$P(x) \simeq \exp\left(-\frac{1}{\epsilon^2}V(x)\right), \tag{1·4}$$

where $V(x) = I_\infty(\phi_t^*)$ with ϕ_t^* a trajectory connecting the equilibrium point to x and minimizing I_∞. If there are several equilibrium points or attractors the theory can be easily extended.

The lesson we learn is that in the limit of small noise an estimate of the stationary distribution is reduced to the solution of a variational problem.

Equation (1.4) reminds of the Einstein theory of equilibrium thermodynamic fluctuations[2),3)] which states that the probability of a fluctuation from equilibrium in a macroscopic region of volume V is proportional to

$$\exp\{V\Delta S/k\},$$

where ΔS is the variation of entropy density calculated along a reversible transformation creating the fluctuation and k is the Boltzmann constant. This theory is well established and has received a rigorous mathematical formulation in classical equilibrium statistical mechanics.[4)] The analogy with Einstein formula is especially

suggestive: establishing estimates of this kind in nonequilibrium leads naturally to the identification of the exponent with a nonequilibrium thermodynamic function. Clearly the role of the small parameter ϵ is taken by the inverse of the volume. This is the starting point of the theory reviewed in this paper. For related approaches see.[5),6)]

§2. Basic equations and the large deviation functional

The following equations characterize the macroscopic behaviour of a wide class of stochastic lattice gases and agree with the phenomenological equations used so far in nonequilibrium thermodynamics near equilibrium, see e.g. the book.[7)]

1. *The macroscopic state is completely described by the local density $\rho = \rho(t,x)$ and the associated current $j = j(t,x)$.*
2. *The macroscopic evolution is given by the continuity equation*

$$\partial_t \rho + \nabla \cdot j = 0, \tag{2·1}$$

together with the constitutive equation

$$j = J(\rho) = -D(\rho)\nabla\rho + \chi(\rho)E, \tag{2·2}$$

where the diffusion coefficient *$D(\rho)$ and the* mobility *$\chi(\rho)$ are $d \times d$ positive matrices. The transport coefficients D and χ satisfy the local Einstein relation*

$$D(\rho) = \chi(\rho)\, f_0''(\rho), \tag{2·3}$$

where f_0 is the equilibrium free energy of the homogeneous system.

The equations (2·1)–(2·2) have to be supplemented by the appropriate boundary conditions on $\partial\Lambda$ due to the interaction with the external reservoirs. If $\lambda_0(x)$, $x \in \partial\Lambda$, is the chemical potential of the external reservoirs, these boundary conditions are

$$f_0'\big(\rho(x)\big) = \lambda_0(x), \qquad x \in \partial\Lambda. \tag{2·4}$$

Some comments are in order. There are no restrictions on the values of the chemical potential or on the nonlinearity so that situations far from equilibrium or from a stationary state are included. We denote by $\bar\rho = \bar\rho(x)$, $x \in \Lambda$, the stationary solution, assumed to be unique, of equations (2·1) to (2.4).

In the constitutive equation (2·2) the external field appears linearly which microscopically means a field of order $1/N$ acting on each particle, where N is the linear dimension of the lattice. A field of order 1 would destroy the diffusive character of the evolution giving rise to a hyperbolic evolution equation of first order.

The transport coefficients D and χ depend in general on the density ρ. In the case the system has more than one component, say n, the diffusion coefficient D and the mobility become $nd \times nd$ matrices. Moreover, in view of Onsager reciprocity, the matrix χ is symmetric both in the space and in the component indices while D is symmetric only in the space indices. In such a case the local Einstein relation (2·3) is $D = \chi R$ where $R_{ij} = \partial_{\rho_i}\partial_{\rho_j} f_0$ does not depend on the space indices.

Summarizing, in the context of stochastic lattice gases, (2·1) and (2·2) describe the evolution of the density in the diffusive scaling limit, see e.g.[8),9)] The validity of the local Einstein relationship (2·3) can be deduced from the local detailed balance of the underlying microscopic dynamics, see e.g.[9)]

So far the analysis of the stochastic models can be viewed as a confirmation of the phenomenological schemes used by physicists and chemists for a long time. The really new information comes from the study of large deviations from the above deterministic macroscopic description.

For a wide class of models the following holds. The stationary measure P_{st} admits a principle of large deviations describing the fluctuations of the thermodynamic variable appearing in the hydrodynamic equation. This means the following. The probability that in a lattice of N^d points the evolution of the so-called empirical density $\rho_N(X_t) = \frac{1}{N^d} \sum_{x \in \Lambda_N} \eta_x(N^2 t) \, \delta\left(u - \frac{x}{N}\right)$, where η_x is the number of particles at site x and X_t is the microscopic configuration, deviates from the solution of the hydrodynamic equation and is close to some trajectory $\hat{\rho}(t)$, is exponentially small and of the form

$$P_{st}\left(\rho_N(X_t) \sim \hat{\rho}(t), t \in [t_1, t_2]\right) \approx e^{-N^d[\mathcal{F}(\hat{\rho}(t_1)) + I_{[t_1,t_2]}(\hat{\rho})]}, \qquad (2·5)$$

where $I(\hat{\rho})$ is a functional which vanishes if $\hat{\rho}(t)$ is a solution of (2·1)–(2·2) and $\mathcal{F}(\hat{\rho}(t_1))$ is the cost to produce the initial density profile $\hat{\rho}(t_1)$. We normalize it so that $\mathcal{F}(\bar{\rho}) = 0$. The functional $I(\hat{\rho})$ represents the extra cost necessary to follow the trajectory $\hat{\rho}(t)$. Finally $\rho_N(X_t) \sim \hat{\rho}(t)$ means closeness in some metric and $\approx$ denotes logarithmic equivalence as $N \to \infty$.

A simple argument based on time reversal[10)] now shows that

$$\mathcal{F}(\rho) = \inf_{\hat{\rho}} I_{[-\infty,0]}(\hat{\rho}), \qquad (2·6)$$

where the inf has to be taken over all trajectories connecting the stationary state $\bar{\rho}$ to the profile ρ. The same argument identifies the minimizing trajectory, see later. The quantity $\mathcal{F}(\rho)$ is an infinite dimensional analog of the $V(x)$ in Freidlin-Ventzell theory and has to be identified with a non equilibrium thermodynamic function. The fluctuations we are considering take place at constant temperature and volume so that it is reasonable to identify $\mathcal{F}(\rho)$ with the variation of the nonequilibrium free energy to produce the profile ρ. If the stationary state is an equilibrium state the Einstein theory is recovered as it will be discussed later.

The explicit formula of the functional $I_{[t_1,t_2]}(\hat{\rho})]$ is

$$I_{[T_1,T_2]}(\hat{\rho}) = \frac{1}{4} \int_{T_1}^{T_2} dt \left\langle \left[\partial_t \hat{\rho} + \nabla \cdot J(\hat{\rho})\right] K(\hat{\rho})^{-1} \left[\partial_t \hat{\rho} + \nabla \cdot J(\hat{\rho})\right] \right\rangle, \qquad (2·7)$$

where the positive operator $K(\hat{\rho})$, the analog of σ^2 in Freidlin-Ventzell theory, is defined on functions u vanishing at the boundary $\partial \Lambda$ by $K(\hat{\rho})u = -\nabla \cdot \left(\chi(\hat{\rho}) \nabla u\right)$. The expression (2.7) is similar to (1.3), i.e. the fluctuations of the thermodynamic variables of a stochastic lattice gas are formally those of a stochastic partial differential

equation where the deterministic part is given by hydrodynamics. These equations are known as *fluctuating hydrodynamics* and are often used in phenomenological calculations. One has to be careful however because it is often difficult to attribute a precise mathematical meaning to stochastic nonlinear partial differential equations. Divergences akin to those in quantum field theory appear in dimension greater than 1.

For a heuristic derivation of (2.7) see.[10] There is factor $1/2$ of difference due to a slightly different definition of the transport coefficients D and χ.

§3. The Hamilton-Jacobi equation and the interpretation of $\mathcal{F}$

As shown in[10],[11] the functional $\mathcal{F}$, as defined in (2.6), is the maximal solution of the infinite dimensional Hamilton-Jacobi equation

$$\left\langle \nabla \frac{\delta \mathcal{F}}{\delta \rho} \cdot \chi(\rho) \nabla \frac{\delta \mathcal{F}}{\delta \rho} \right\rangle - \left\langle \frac{\delta \mathcal{F}}{\delta \rho} \, \nabla \cdot J(\rho) \right\rangle = 0, \tag{3.1}$$

where, for ρ that satisfies (2.4), $\delta\mathcal{F}/\delta\rho$ vanishes at the boundary of Λ. At the macroscopic level this condition reflects the fact that we consider variations of the density that do not change the boundary values. The arbitrary additive constant on the maximal solution of (3.1) is determined by the condition $\mathcal{F}(\bar{\rho}) = 0$. By maximal solution we mean that any solution $F(\rho)$ to (3.1) (satisfying $F(\bar{\rho}) = 0$) is a lower bound for $\mathcal{F}$. In nonequilibrium we expect generically $\mathcal{F}$ to depend nonlocally on the density.

It is easy to see that the Hamilton-Jacobi equation implies that ∇J can be decomposed in such a way that the hydrodynamic equations can be written

$$\partial_t \rho = -\nabla J(\rho) = \nabla \cdot \left(\chi(\rho) \nabla \frac{\delta \mathcal{F}}{\delta \rho} \right) + \mathcal{A}(\rho), \tag{3.2}$$

where $\mathcal{A}(\rho)$ satisfies the orthogonality condition

$$\left\langle \frac{\delta \mathcal{F}}{\delta \rho} \, , \, \mathcal{A}(\rho) \right\rangle = 0. \tag{3.3}$$

This decomposition confirms the interpretation of $\mathcal{F}$ as a nonequilibrium free energy. In fact the first term is the dissipative part of the equation which determines the relaxation to the stationary state due to the thermodynamic force $\nabla \frac{\delta \mathcal{F}}{\delta \rho}$ while $\mathcal{A}(\rho)$ does not contribute to the spontaneous relaxation. $\mathcal{A}(\rho)$ is minus the divergence of the non-dissipative part of the current and vanishes in the stationary state. It can be shown that[10] the hydrodynamics associated to the time reversed microscopic process can be written

$$\partial_t \rho = -\nabla J^*(\rho) = \nabla \cdot \left(\chi(\rho) \nabla \frac{\delta \mathcal{F}}{\delta \rho} \right) - \mathcal{A}(\rho), \tag{3.4}$$

where $J^*(\rho)$ is the current associated to the time reversed process. By summing equations (3.2) and (3.4) we obtain the nonequilibrium fluctuation-dissipation relation

$$\nabla(J^*(\rho) + J(\rho)) = -2\nabla\chi(\rho)\nabla\frac{\delta\mathcal{F}}{\delta\rho}. \tag{3.5}$$

Actually a similar relation holds for the currents[12]

$$J^*(\rho) + J(\rho) = -2\chi(\rho)\nabla\frac{\delta\mathcal{F}}{\delta\rho}. \tag{3.6}$$

We can now identify the optimal (minimizing) trajectory in (2.6). Let $\mathcal{F}$ be the maximal solution of the Hamilton-Jacobi equation and J^* as in (3.6). Fix a time interval $[T_1, T_2]$ and a path $\hat{\rho}(t)$, $t \in [T_1, T_2]$. We claim that

$$I_{[T_1,T_2]}(\hat{\rho}) = \mathcal{F}(\hat{\rho}(T_2)) - \mathcal{F}(\hat{\rho}(T_1))$$
$$+ \frac{1}{4}\int_{T_1}^{T_2} dt\, \left\langle \left[\partial_t\hat{\rho} - \nabla\cdot J^*(\hat{\rho})\right] K(\hat{\rho})^{-1}\left[\partial_t\hat{\rho} - \nabla\cdot J^*(\hat{\rho})\right]\right\rangle, \tag{3.7}$$

as can be shown by a direct computation using (2.7), the Hamilton-Jacobi equation (3.1) and (3.6). From the identity (3.7) we immediately deduce that the optimal path for the variational problem (2.6) is the time reversal of the solution to (3.4) with initial condition ρ.

We next show that according to definition (2.6), the free energy $\mathcal{F}(\rho)$ is equal to the work done by the thermodynamic force on the system along the optimal trajectory ρ^*. Indeed, by the above identification of ρ^*

$$\mathcal{F}(\rho) - \mathcal{F}(\bar{\rho}) = \int_{-\infty}^{0} dt\, \left\langle \frac{\delta\mathcal{F}}{\delta\rho}, \partial_t\rho^*\right\rangle$$
$$= \int_{-\infty}^{0} dt\, \left\langle \frac{\delta\mathcal{F}}{\delta\rho}, \nabla\cdot J^*(\rho^*)\right\rangle = \int_{-\infty}^{0} dt\, \left\langle (-J^*(\rho^*))\cdot\nabla\frac{\delta\mathcal{F}}{\delta\rho}\right\rangle.$$

The decompositions (3.2)-(3.4) remind of the electrical conduction in presence of a magnetic field.[13] Consider the motion of electrons in a conductor: a simple model is given by the effective equation,[14]

$$\dot{\mathbf{p}} = -e\left(\mathbf{E} + \frac{1}{mc}\mathbf{p}\wedge\mathbf{H}\right) - \frac{1}{\tau}\mathbf{p}, \tag{3.8}$$

where $\mathbf{p}$ is the momentum, e the electron charge, $\mathbf{E}$ the electric field, $\mathbf{H}$ the magnetic field, m the mass, c the velocity of the light, and τ the relaxation time. The dissipative term $\mathbf{p}/\tau$ is orthogonal to the Lorenz force $\mathbf{p}\wedge\mathbf{H}$. We define time reversal as the transformation $\mathbf{p}\mapsto-\mathbf{p}$, $\mathbf{H}\mapsto-\mathbf{H}$. The time reversed evolution is given by

$$\dot{\mathbf{p}} = e\left(\mathbf{E} + \frac{1}{mc}\mathbf{p}\wedge\mathbf{H}\right) - \frac{1}{\tau}\mathbf{p}. \tag{3.9}$$

Let us consider in particular the Hall effect where we have conduction along a rectangular plate immersed in a perpendicular magnetic field H with a potential difference across the long side. The magnetic field determines a potential difference across the short side of the plate. In our setting on the contrary it is the difference in chemical potentials at the boundaries that introduces in the equations a non-dissipative term.

§4. Equilibrium states and macroscopic reversibility

In this section we consider the notion of *equilibrium* from the standpoint of *nonequilibrium*.[15)] We define the system to be in *equilibrium* if and only if the current in the stationary profile $\bar{\rho}$ vanishes, i.e. $J(\bar{\rho}) = 0$. Nonetheless, in presence of external (electric) fields and boundary reservoirs an equilibrium state can be highly inhomogeneous. An example of such a situation is provided by sedimentation equilibrium in gravitational and centrifugal fields. In spite of this, the free energy is a local function of the state variables and coincides locally with the equilibrium free energy in absence of external fields and boundary driving. In particular there are no macroscopic correlations.

For an equilibrium state, characterized by a constant or non constant stationary profile $\bar{\rho}(x)$ such that $J(\bar{\rho}) = 0$, the free energy functional $\mathcal{F}$ is obtained as follows. Let

$$f(\rho, x) = \int_{\bar{\rho}(x)}^{\rho} dr \int_{\bar{\rho}(x)}^{r} dr' \, f_0''(r') = f_0(\rho) - f_0(\bar{\rho}(x)) - f_0'\big(\bar{\rho}(x)\big)\big[\rho - \bar{\rho}(x)\big],$$

where, we recall, $f_0(\rho)$ is the equilibrium free energy density. It is easy to show[15)] that the maximal solution of the Hamilton-Jacobi equation is

$$\mathcal{F}(\rho) = \int_{\Lambda} dx \, f\big(\rho(x), x\big). \tag{4.1}$$

We emphasize that the above argument depends crucially on the structure (2·2) of the current and on validity of the local Einstein relation (2·3).

The condition $J(\bar{\rho}) = 0$ can be shown[15)] to be equivalent to $J^*(\rho) = J(\rho)$ for any profile ρ. We call the latter condition *macroscopic reversibility*. The notion of macroscopic reversibility does not imply that an underlying microscopic model satisfies the detailed balance condition. Indeed, as it has been shown by explicit examples,[16), 17)] there are non reversible microscopic models which are macroscopically reversible. If the system is macroscopically reversible the optimal trajectory to create a fluctuation is the time reversal of the relaxation trajectory solution of (2·1)-(2·2). In[10)] we called this symmetry the Onsager-Machlup time reversal symmetry.[18), 19)] We have defined the macroscopic reversibility as the identity between the currents $J(\rho)$ and $J^*(\rho)$. We emphasize that this is not equivalent to the identity between $\nabla \cdot J(\rho)$ and $\nabla \cdot J^*(\rho)$. Indeed, it is possible to give examples[15)] of a non reversible system, i.e. with $J(\bar{\rho}) \neq 0$, such that the optimal trajectory for the variational problem (2.6) is the time reversal of the solution to the hydrodynamic equation (2·1)-(2·2).

Our analysis of equilibrium so far does not include magnetic fields but can be extended to cover this situation. It can be done by distinguishing dissipative and non dissipative currents: a natural definition of equilibrium is then the vanishing of the dissipative currents.

§5. Long range correlations

Space correlations extending over macroscopic distances appear to be a generic feature of stationary nonequilibrium states, a fact known since a long time.[20),21)] The ultimate reason for these correlations seems to be connected with the violation of time reversal as they can appear also in equilibrium states if the microscopic dynamics *strongly* violates time reversal invariance.[22),23)] An interesting question is to what extent long range correlations make nonequilibrium akin to critical phenomena.

In our approach, since we are not limited to the vicinity of the stationary state we can obtain the (nonequilibrium) density correlations functions of arbitrary order in terms of the functional derivatives of $\mathcal{F}$. In general the functional $\mathcal{F}$ cannot be written in a closed form, but - by a suitable perturbation theory on the Hamilton-Jacobi equation (3·1) - we can derive such correlations functions. In this section we discuss the two-point correlation and establish a criterion to decide whether the density fluctuations are positively or negatively correlated. Recursive equations for the correlation functions of any order are established in.[15)] We emphasize that we are concerned only with *macroscopic correlations* which are a generic feature of nonequilibrium models. Microscopic correlations which decay exponentially or as a summable power law disappear at the macroscopic level.

We introduce the *pressure* functional as the Legendre transform of free energy $\mathcal{F}$

$$\mathcal{G}(h) = \sup_{\rho} \big\{ \langle h\rho \rangle - \mathcal{F}(\rho) \big\}.$$

By Legendre duality we have the change of variable formula $h = \frac{\delta\mathcal{F}}{\delta\rho}$, $\rho = \frac{\delta\mathcal{G}}{\delta h}$, so that the Hamilton-Jacobi equation (3·1) can be rewritten in terms of $\mathcal{G}$ as

$$\Big\langle \nabla h \cdot \chi\Big(\frac{\delta\mathcal{G}}{\delta h}\Big)\nabla h \Big\rangle - \Big\langle \nabla h \cdot D\Big(\frac{\delta\mathcal{G}}{\delta h}\Big)\nabla\frac{\delta\mathcal{G}}{\delta h} - \chi\Big(\frac{\delta\mathcal{G}}{\delta h}\Big)E \Big\rangle = 0, \qquad (5·1)$$

where h vanishes at the boundary of Λ. As for equilibrium systems, $\mathcal{G}$ is the generating functional of the correlation functions. In particular, by defining

$$C(x,y) = \frac{\delta^2\mathcal{G}(h)}{\delta h(x)\delta h(y)}\Big|_{h=0}.$$

we have, since $\mathcal{F}$ has a minimum at $\bar{\rho}$,

$$\mathcal{G}(h) = \langle h, \bar{\rho} \rangle + \frac{1}{2}\langle h, Ch \rangle + o(h^2),$$

or equivalently

$$\mathcal{F}(\rho) = \frac{1}{2}\langle (\rho - \bar{\rho}), C^{-1}(\rho - \bar{\rho}) \rangle + o((\rho - \bar{\rho})^2).$$

By expanding the Hamilton-Jacobi equation (5·1) to the second order in h, and using that $\delta\mathcal{G}/\delta h(x) = \bar{\rho}(x) + Ch(x) + o(h^2)$, we get the following equation for C

$$\Big\langle \nabla h \cdot \Big[\chi(\bar{\rho})\nabla h - \nabla(D(\bar{\rho})Ch) + \chi'(\bar{\rho})(Ch)E \Big] \Big\rangle = 0. \qquad (5·2)$$

We now make the change of variable

$$C(x, y) = C_{\text{eq}}(x)\delta(x - y) + B(x, y),$$

where $C_{\text{eq}}(x)$ is the equilibrium covariance. By using (2·3) we deduce that

$$C_{\text{eq}}(x) = D^{-1}(\bar{\rho}(x))\chi(\bar{\rho}(x)).$$

Equation (5·2) for the correlation function then gives the following equation for B

$$\mathcal{L}^{\dagger}B(x, y) = \alpha(x)\delta(x - y), \tag{5·3}$$

where $\mathcal{L}^{\dagger}$ is the formal adjoint of the elliptic operator $\mathcal{L} = L_x + L_y$ given by, using the usual convention that repeated indices are summed,

$$L_x = D_{ij}(\bar{\rho}(x))\partial_{x_i}\partial_{x_j} + \chi'_{ij}(\bar{\rho}(x))E_j(x)\partial_{x_i}, \tag{5·4}$$

and

$$\alpha(x) = \partial_{x_i}\big[\chi'_{ij}\big(\bar{\rho}(x)\big)\, D_{jk}^{-1}\big(\bar{\rho}(x)\big)\,\bar{J}_k(x)\big],$$

where we recall $\bar{J} = J(\bar{\rho}) = -D(\bar{\rho}(x))\nabla\bar{\rho}(x) + \chi(\bar{\rho}(x))E(x)$ is the macroscopic current in the stationary profile.

In equilibrium systems $\bar{J} = 0$ so that we have $\alpha = 0$, hence $B = 0$, namely there are no long range correlations and $C(x, y) = C_{\text{eq}}(x)\delta(x - y)$. Moreover, since $\mathcal{L}$ is an elliptic operator (i.e. it has a negative kernel), the sign of B is determined by the sign of α: if $\alpha(x) \geq 0, \forall x$, then $B(x, y) \leq 0, \forall x, y$, while if $\alpha(x) \leq 0, \forall x$, then $B(x, y) \geq 0, \forall x, y$. For example, consider the following special case. The system is one-dimensional, $d = 1$, the diffusion coefficient is constant, i.e. $D(\rho) = D_0$, the mobility $\chi(\rho)$ is a quadratic function of ρ, and there is no external field, $E = 0$. Then

$$B(x, y) = -\frac{1}{2D_0}\chi''(\nabla\bar{\rho})^2\Delta^{-1}(x, y), \tag{5·5}$$

where $\Delta^{-1}(x, y)$ is the Green function of the Dirichlet Laplacian. Two well studied models, the symmetric exclusion process, where $\chi(\rho) = \rho(1 - \rho)$, and the KMP process,[25] where $\chi(\rho) = \rho^2$, meet the above conditions. Then (5·5) shows that their correlations have opposite signs.

§6. Thermodynamics of currents

In nonequilibrium a very important observable is the current flux. This quantity gives information that cannot be recovered from the density because from a density trajectory we can determine the current trajectory only up to a divergence free vector field. To discuss the current fluctuations, we introduce a vector-valued observable $\mathcal{J}_N(\{X_\sigma, 0 \leq \sigma \leq \tau\})$ of the microscopic trajectory X_t which measures the local net flow of particles and satisfies formally the microscopic continuity equation

$$\partial_t\rho_N + \nabla_N \cdot \mathcal{J}_N = 0,$$

where ∇_N is the gradient on the lattice. For the details see.[12),24)] As in the case of the density, for stochastic lattice gases, we are able to derive a dynamical large deviations principle for the current. If P_{X_0} stands for the probability P_{st} conditioned on the initial microscopic state X_0, given a vector field $j : [0, T] \times \Lambda \to \mathbb{R}^d$, we have

$$P_{X_0}\big(\mathcal{J}_N(X) \approx j(t, u)\big) \sim \exp\big\{ - N^d \mathcal{I}_{[0,T]}(j)\big\}, \qquad (6\cdot1)$$

where the rate functional is

$$\mathcal{I}_{[0,T]}(j) \;=\; \frac{1}{4}\int_0^T dt \,\big\langle [j - J(\rho)], \chi(\rho)^{-1}[j - J(\rho)]\big\rangle. \qquad (6\cdot2)$$

We recall that

$$J(\rho) = -D(\rho)\nabla\rho + \chi(\rho)E \;.$$

In (6·2) $\rho = \rho(t, u)$ is the solution of the continuity equation $\partial_t \rho + \nabla \cdot j = 0$ with the initial condition $\rho(0) = \rho_0$ associated to X_0. The rate functional vanishes if $j = J(\rho)$.

Among the many problems we can discuss within this theory, the fluctuations of the time average of the current $\mathcal{J}_N$ over a large time interval have been analysed. This question was addressed by Bodineau and Derrida in[26)] in one space dimension by postulating an *"additivity principle"* which relates the fluctuation of the time averaged current in the whole system to the fluctuations in subsystems. However their approach does not always apply. In fact the probability of observing a given divergence free time averaged fluctuation J can be described by a functional $\Phi(J)$ which we characterize, in any dimension, in terms of a variational problem for the functional $\mathcal{I}_{[0,T]}$

$$\Phi(J) = \lim_{T\to\infty} \inf_j \frac{1}{T}\,\mathcal{I}_{[0,T]}(j) \;, \qquad (6\cdot3)$$

where the infimum is carried over all paths $j = j(t, u)$ having time average J. The static additivity principle postulated in[26)] gives the correct answer only under additional hypotheses which are not always satisfied. Let us denote by U the functional obtained by restricting the infimum in (6·3) to divergence free current paths j, i.e.

$$U(J) = \inf_\rho \frac{1}{4}\big\langle [J - J(\rho)], \chi(\rho)^{-1}[J - J(\rho)]\big\rangle, \qquad (6\cdot4)$$

where the infimum is carried out over all the density profiles $\rho = \rho(u)$ satisfying the appropriate boundary conditions. From (6·3) and (6·4) it follows that $\Phi \leq U$. In one space dimension the functional U is the one introduced in.[26)] While Φ is always convex the functional U may be non convex. In such a case $U(J)$ underestimates the probability of the fluctuation J. In[12),24)] we interpreted the lack of convexity of U, and more generally the strict inequality $\Phi < U$, as a dynamical phase transition.

There are cases in which $\Phi = U$. Sufficient conditions on the transport coefficients D, χ for the coincidence of Φ and U can be given.[12)] Consider the case when the matrices $D(\rho)$ and $\chi(\rho)$ are multiples of the identity, i.e., there are strictly positive scalar functions still denoted by $D(\rho)$, $\chi(\rho)$, so that $D(\rho)_{i,j} = D(\rho)\delta_{i,j}$,

$\chi(\rho)_{i,j} = \chi(\rho)\delta_{i,j}$, $i, j = 1, \ldots, d$. Let us first consider the case with no external field, i.e. $E = 0$; if

$$D(\rho)\chi''(\rho) \leq D'(\rho)\chi'(\rho), \quad \text{for any } \rho, \tag{6\cdot5}$$

where $'$ denotes the derivative, then $\Phi = U$. In this case U is necessarily convex. Moreover if

$$D(\rho)\chi''(\rho) = D'(\rho)\chi'(\rho), \quad \text{for any } \rho, \tag{6\cdot6}$$

then we have $\Phi = U$ for any external field E.

To exemplify situations in which $\Phi < U$ consider the fluctuations of the time averaged current for periodic boundary conditions. Two models have been discussed so far. The Kipnis–Marchioro-Presutti (KMP) model,[27] which is defined by a harmonic chain with random exchange of energy between neighboring oscillators, and the exclusion process. In the case of the KMP model we have $U(J) = (1/4)J^2/\chi(m) = (1/4)J^2/m^2$, where m is the (conserved) total energy. For J large enough, $\Phi(J) < U(J)$. This inequality is obtained by constructing a suitable travelling wave current path whose cost is less than $U(J)$.[12] For J not too large the additivity principle holds as it has been verified numerically in.[28] A similar result has been obtained by Bodineau and Derrida[29] for the periodic simple exclusion process with external field. For the KMP process this phenomenon is rather striking as it occurs even in equilibrium, i.e. without external field.

The behavior of $\mathcal{I}$ and Φ under time reversal shows that Φ satisfies a fluctuation relationship akin to the Gallavotti-Cohen theorem for the entropy production.[30]–[32] The anti-symmetric part of Φ is equal to the power produced by the external field and the reservoirs independently of the details of the model

$$\Phi(J) - \Phi(-J) = \Phi(J) - \Phi^a(J) = -2\langle J, E \rangle + \int_{\partial\Lambda} d\Sigma \, \lambda_0 \, J \cdot \hat{n}, \tag{6\cdot7}$$

the right hand side of this equation is the power produced by the external field and the boundary reservoirs (recall E is the external field and λ_0 the chemical potential of the boundary reservoirs). From this relationship one derives a macroscopic version of the fluctuation theorem for the entropy production.

For recent interesting results obtained from the macroscopic fluctuation theory in the study of current fluctuations see.[33],[34]

§7. Conclusions and comparison with other approaches

The theory developed so far, as emphasized in,[15] can be viewed as a selfcontained macroscopic description of diffusive systems out of equilibrium. It allows a clear identification of the dissipative part and of thermodynamic forces in relaxation phenomena. Long range space correlations among thermodynamic variables are a generic consequence of the theory and equations for the correlation functions of any order have been established.[15] Also different regimes in current fluctuations are predicted that have been characterized as dynamical phase transitions. These transitions are shown to exist in the simplest models considered and it is a challenge to discover them in real systems.

The thermodynamic functionals $\mathcal{F}$ and Φ can be calculated from dynamical measurable quantities like the transport coefficients D and χ. This is a deep difference with respect to equilibrium thermodynamics where static properties like specific heats are involved. From the standpoint of nonequilibrium it is natural to consider also the equilibrium free energy as determined by the transport coefficients through the Einstein relation.

Another substantial difference is that in the definition of nonequilibrium thermodynamic functionals optimal trajectories are involved which are different from the infinitely slow reversible transformations of classical thermodynamics: the optimal trajectories go through nonequilibrium nonstationary states. In the theory developed so far the boundary conditions are kept fixed: the study under boundary conditions (chemical potentials, volume...) which slowly vary on the macroscopic time scale is a next natural step.

A different very general approach to the theory of nonequilibrium stationary states was initiated by Oono and Paniconi[35] and pursued in the work of Hatano, Hayashi, Sasa, Tasaki.[36]–[38] While in[36],[37] microscopic models underlie the analysis, in[38] a guiding idea is to keep as much as possible the phenomenological character of classical thermodynamics without reference to an underlying microscopic dynamics. In this work the authors discuss the operational definition of nonequilibrium thermodynamic observables in concrete situations and generalize basic operations like decomposition, combination and scaling of equilibrium thermodynamics to nonequilibrium states. The possibility of experimental tests is then discussed.

In more recent papers by Komatsu, Nakagawa[39] and by Komatsu, Nakagawa, Sasa, Tasaki,[40],[41] the problem of constructing microscopic ensembles describing stationary states of both stochastic and Hamiltonian systems, is considered. Expressions for the nonequilibrium distribution function are proposed either exact or valid up to a certain order in the parameters keeping the system out of equilibrium. The key quantity appearing in these expressions is the entropy production. In[40] heat conduction is considered in particular and an extension of the Clausius and Gibbs relations is derived.

A direct comparison between these works and ours is not immediately available as we are asking different questions but an effort should be made to construct a bridge between them.

In a recent paper Öttinger[42] compared his own approach[43] to nonequilibrium, called GENERIC (general equation for the nonequilibrium reversible-irreversible coupling), with our macroscopic fluctuation theory discussing aspects where a correspondence could be established. His starting point is a separation in the macroscopic evolution equations of dissipative and conservative terms which reminds of our decomposition (3.2). An important difference is related to the fact that our free energy out of equilibrium is generically nonlocal in space and this is connected with the existence of long range correlations. There is more to understand and the comparison should be developed further.

Acknowledgements

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